

Di- μ -aqua-bis[(*N*-salicylidene- β -alaninato- κ^3O,N,O')copper(II)] urea disolvate

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Received 4 March 2004

Accepted 2 April 2004

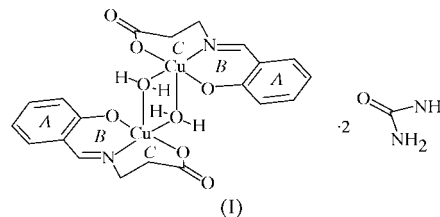
Online 22 May 2004

Crystals of the title compound, $[\text{Cu}_2(\text{C}_{10}\text{H}_9\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 2\text{CH}_4\text{N}_2\text{O}$, consist of two (*N*-salicylidene- β -alaninato- κ^3O,N,O')copper(II) coordination units bridged by two water moieties to form a dimer residing on a crystallographic inversion center, along with two uncoordinated urea molecules. The Cu^{II} atom has square-pyramidal coordination, with three donor atoms of the tridentate Schiff base and an O atom of the bridging aqua ligand in the basal plane. The axial position is occupied by the second bridging water ligand at a distance of 2.5941 (18) Å. Hydrogen bonds between molecules of urea and the neighboring dimer units lead to the formation of a two-dimensional grid of molecules parallel to [101]. The superposition of the normals of the pyramidal base planes in the direction [100] indicates possible π - π interactions between the neighboring units.

Comment

Cu^{II} centers coordinated by *O,N,O'*-tridentate Schiff base dianions (TSBs) derived from salicylaldehyde and amino acids can form a variety of chelates by filling out the coordination environment, resulting in a square-planar (Warda, 1997a; Warda *et al.*, 1997), square-pyramidal (Kettmann *et al.*, 1993; Hill & Warda, 1999; Weng *et al.*, 2002; Butcher *et al.*, 2003; Vančo *et al.*, 2003) or distorted square-bipyramidal polyhedron (Marek *et al.*, 2003), or in a mixed square-pyramidal/square-planar form (Werner *et al.*, 1983). Depending on the proportions and physicochemical properties of the additional ligands, monomeric (Warda, 1997a,b, 1998a,b), dimeric (Werner *et al.*, 1983; Warda, 1998c; Hill & Warda, 1999; Vančo *et al.*, 2003), oligomeric (Warda, 1997c) or polymeric (Warda *et al.*, 1997; Warda, 1998d; Kettmann *et al.*, 1993) crystal structures are formed. One of the features specific to $\text{Cu}(\text{TSB})$ complexes is

stabilization of the oxidation number of Cu^{II} , as demonstrated in the case of thiourea- $\text{Cu}(\text{TSB})$ complexes (Švajlenová & Krátsmár-Šmogrovič, 1978; Pavelčík *et al.*, 1981; Warda *et al.*, 1998) and cuprates with thiocyanate ions in the inner coordination sphere of the Cu^{II} atom (Sivý *et al.*, 1990; Kettmann *et al.*, 1992; Marek *et al.*, 2003; Vančo *et al.*, 2003).



The unique distorted square-pyramidal arrangement around the Cu^{II} atom also gives $\text{Cu}(\text{TSB})$ complexes the potential to act as antiradical (Bergendi *et al.*, 1991; Valentová, Žemlička *et al.*, 1995), radioprotective (Valentová, Gombo *et al.*, 1995) and antimicrobial agents (Sokolík *et al.*, 1997), and as inhibitors of enzymatic systems (Kráľová *et al.*, 2004). In the present and in recent studies, the greatest emphasis was given to the Schiff base chelates with additional molecular N-ligands, mostly derived from pyridine, imidazole, pyrazole or quinoline. Only a few papers have dealt with the structural characterization or biological activity of urea complexes, where urea usually acts as an O-ligand (Warda *et al.*, 1998; Valent *et al.*, 2002). These studies introduced the structures of urea(*N*-salicylidene-glycinato)copper(II) and urea(*N*-salicylidene-methylalaninato)copper(II), and the antimicrobial potential of the former was mentioned. From the structural point of view, the urea ligand offers the possibility of forming an extensive hydrogen-bonding network through the involvement of two non-coordinated NH_2 groups. In light of the biological activities mentioned above and their relationship to structural properties, the title compound, (I), was synthesized and studied.

The dimer of (I) consists of two $[\text{Cu}(\text{sal-}\beta\text{-ala})(\text{H}_2\text{O})]$ coordination units spanning a crystallographic inversion center (Fig. 1). The unique Cu^{II} atom adopts a (4+1) square-

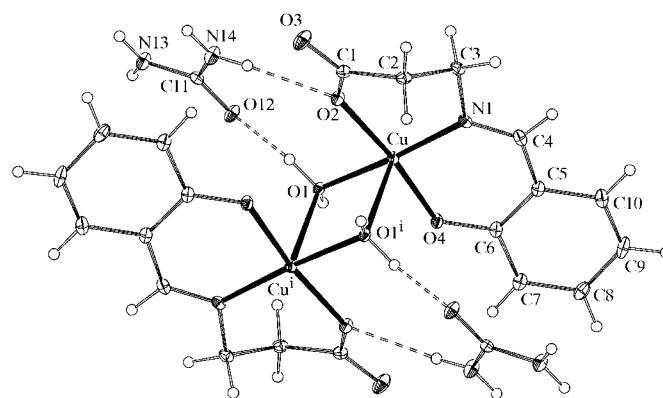


Figure 1

View of the title dimer. Non-H atoms are drawn as 50% probability displacement ellipsoids and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $1 - x, 1 - y, -z$.]

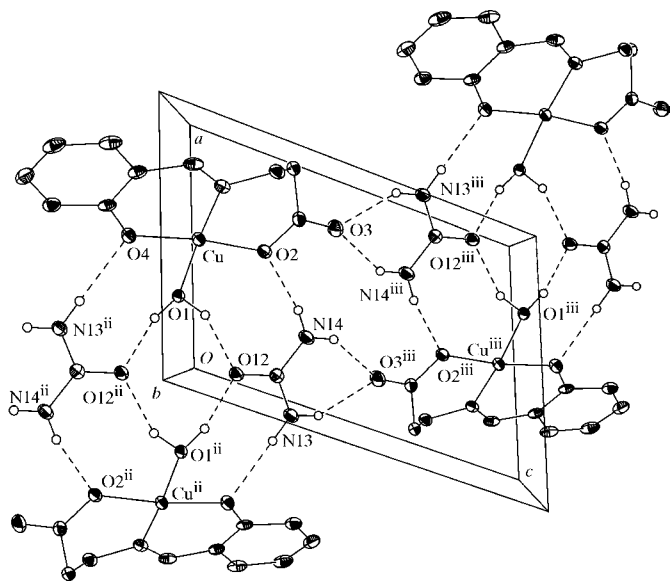


Figure 2
Part of the crystal structure of (I), showing the formation of the hydrogen-bonding network. Only the independent parts of the Cu dimers are shown for clarity. [Symmetry codes: (ii) $-x, 1-y, -z$; (iii) $1-x, 1-y, 1-z$.]

pyramidal geometry, formed by an *O,N,O'*-tridentate *N*-salicylidene- β -alaninate dianion and the water O atom in the basal plane (selected geometric parameters are given in Table 1). The apical position is occupied by the water Oⁱ atom from the second unit [symmetry code: (i) $1-x, 1-y, -z$]. The resulting $[\text{Cu}(\text{sal-}\beta\text{-ala})(\text{H}_2\text{O})]_2$ dimer, containing two bridging aqua molecules fixed in their positions by a grid of hydrogen bonds, is a structural motive observed for the first time in *N*-salicylideneamino acid copper(II) complexes. The structure of (I) thus differs significantly from the structure of the starting material $[\text{Cu}_2(\text{sal-}\beta\text{-ala})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, (II) (Werner *et al.*, 1983), where the dimer is formed by two coordination units connected *via* two Cu–O bonds to bridging phenolate O atoms of the adjacent unit at distances of 1.986 and 2.013 Å. In addition, the Cu^{II} coordination polyhedra in (I) and (II) are different. The polyhedra of the two Cu^{II} atoms in (II) have distorted square-planar and square-pyramidal configurations, with the apical position occupied by the water molecule and a Cu–O distance of 2.295 Å, while the coordination polyhedra of the two central atoms in (I) are uniformly square-pyramidal. The equatorial Cu–O1(water) bond distance in the basal plane of the pyramid in (I) decreased to 1.9922 (18) Å and the apical Cu–O1ⁱ bond distance increased to 2.5941 (18) Å, resembling a Jahn–Teller effect. The Cu–water lengths are comparable to the average lengths (1.95 and 2.43 Å) of these bonds in related Cu complexes reported in the Cambridge Structural Database (Version 5.24.3; Allen, 2002).

The pyramidal basal plane is nearly planar; only the Cu atom and two opposite O atoms (O2 and O4) are shifted slightly from the mean plane through the four basal atoms (all deviations are in the range 0.04–0.05 Å) in one direction, and

the remaining two basal atoms are shifted in the opposite direction. In addition, the benzene (labeled *A* in the chemical diagram) and the first six-membered metalochelate ring (labeled *B*) of the sal- β -ala moiety are nearly planar (the mean deviations of the contributing atoms from the least-squares planes are 0.022 and 0.033 Å, respectively), while the second six-membered chelate ring (ring *C*) is significantly deformed; atoms C1 and C2 are displaced by 0.548 (3) and 1.049 (3) Å, respectively, from the mean plane through the remaining four atoms (the mean deviation from the plane is 0.016 Å). The Cremer & Pople (1975) puckering parameters for ring *C* have the values $Q = 0.668$ (2) Å, $\theta = -154.4$ (4) $^\circ$ and $\varphi_2 = 78.7$ (2) $^\circ$. The angle between the planes of rings *A* and *B*, and the angle between the plane of ring *B* and the planar part of ring *C*, are 6.45 (7) and 3.04 (5) $^\circ$, respectively.

In the extended structure of (I), the complex dimers and urea molecules are linked by a network of hydrogen bonds (Table 2 and Fig. 2) into a two-dimensional grid of molecules parallel to [101]. The two shortest hydrogen bonds [O \cdots O = 2.688 (3) and 2.656 (2) Å] connect the urea O atom and the two μ -aqua ligands of two adjacent complexes. The hydrogen bond involving the N14–H14A group as donor is bifurcated.

The chelate ring system resulting from the Schiff base ligand coordination is a suitable electronic system for metalloaromaticity (Masui, 2001) and related interactions. Crystals of (I) exhibit superposition of pyramidal base planes, with possible π – π interactions in the [100] direction.

Experimental

The title compound was prepared by reaction of the corresponding aqua complex (Werner *et al.*, 1983) with an excess of urea in an ethanol–water solution. $\text{Cu}(\text{sal-}\beta\text{-ala})(\text{H}_2\text{O})$ (10 mmol, 2.72 g) and urea (40 mmol, 2.4 g) were added to ethanol–water (120 ml, 3:1 *v/v*) and the mixture was heated to 333 K and stirred vigorously for 60 min until the solid phase disappeared. The solution was filtered and allowed to cool to room temperature. The resulting dark-blue well developed crystals were isolated and analyzed. Analysis (Carlo Erba 1180 instrument) calculated for $\text{C}_{11}\text{H}_{15}\text{CuN}_3\text{O}_5$: C 39.70, H 4.54, N 12.63%; found: C 39.82, H 4.59, N 12.70%.

Crystal data

$[\text{Cu}_2(\text{C}_{10}\text{H}_9\text{NO}_3)_2\cdot(\text{H}_2\text{O})_2]\cdot 2\text{CH}_4\text{N}_2\text{O}$
 $M_r = 665.62$
Triclinic, $P\bar{1}$
 $a = 7.3218$ (10) Å
 $b = 9.0547$ (14) Å
 $c = 10.7935$ (15) Å
 $\alpha = 105.638$ (13) $^\circ$
 $\beta = 108.079$ (12) $^\circ$
 $\gamma = 98.697$ (12) $^\circ$
 $V = 633.14$ (18) Å³

$Z = 1$
 $D_x = 1.746$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 1272 reflections
 $\theta = 3.0$ – 26.4 $^\circ$
 $\mu = 1.75$ mm⁻¹
 $T = 120$ (2) K
Needle, dark blue
 $0.60 \times 0.15 \times 0.05$ mm

Data collection

Kuma KM-4-Plus CCD diffractometer
 ω scans
Absorption correction: analytical (CrysAlis RED; Oxford Diffraction, 2002)
 $T_{\text{min}} = 0.458$, $T_{\text{max}} = 0.882$
4325 measured reflections

2210 independent reflections
1941 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$
 $\theta_{\text{max}} = 25.0$ $^\circ$
 $h = -7 \rightarrow 8$
 $k = -10 \rightarrow 10$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.083$
 $S = 1.01$
 2210 reflections
 181 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0577P)^2 + 0.1P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.60 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.46 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cu—O4	1.9046 (18)	Cu—O1	1.9922 (18)
Cu—O2	1.9417 (18)	Cu—O1 ¹	2.5941 (18)
Cu—N1	1.942 (2)		
O4—Cu—O2	171.49 (7)	O4—Cu—O1 ¹	89.27 (7)
O4—Cu—N1	94.28 (8)	O2—Cu—O1 ¹	90.47 (7)
O2—Cu—N1	94.14 (8)	N1—Cu—O1 ¹	100.16 (7)
O4—Cu—O1	87.02 (7)	O1—Cu—O1 ¹	85.79 (7)
O2—Cu—O1	84.48 (7)	Cu—O1—Cu ¹	94.21 (7)
N1—Cu—O1	173.92 (8)		

Symmetry code: (i) $1 - x, 1 - y, -z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1W \cdots O12	0.92	1.84	2.688 (3)	153
O1—H1V \cdots O12 ⁱⁱ	0.92	1.76	2.656 (2)	165
N14—H14A \cdots O2	0.88	2.16	3.022 (3)	167
N14—H14B \cdots O3 ⁱⁱⁱ	0.88	2.11	2.895 (3)	148
N13—H13A \cdots O4 ⁱⁱ	0.88	2.16	3.022 (3)	167
N13—H13B \cdots O3 ⁱⁱⁱ	0.88	2.10	2.891 (3)	149

Symmetry codes: (ii) $-x, 1 - y, -z$; (iii) $1 - x, 1 - y, 1 - z$.

H atoms were positioned geometrically, with N—H distances of 0.88 Å, C—H distances in the range 0.95–0.99 Å and O—H distances of 0.92 Å, and refined as riding, with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}$ of the parent atom.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Johnson & Burnett, 1996); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997) and *PARST* (Nardelli, 1995).

Financial support of this work by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic (VEGA 1/0508/03), by the Grant Agency of the Czech Republic (GAČR) (grant No. 203/02/0436) and by the Ministry of Education of the Czech Republic (MSM 163700003 and MSM 143100008) is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1055). Services for accessing these data are described at the back of the journal.

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